Calculation of simultaneous chemical and phase equilibrium by the methodof Lagrange multipliers

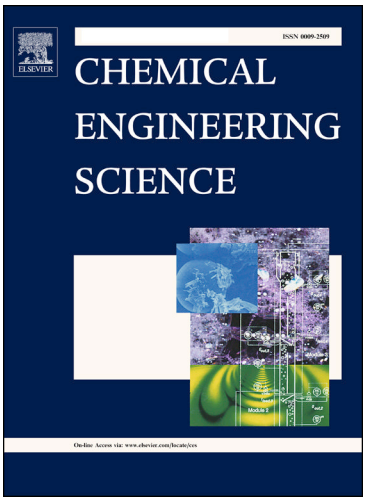
Tsanas, Christos ; Stenby, Erling Halfdan; Yan, Wei

Published in:
Chemical Engineering Science

Link to article, DOI:
10.1016/j.ces.2017.08.033

Publication date:
2017

Document Version
Peer reviewed version



Calculation of Simultaneous Chemical and Phase Equilibrium by the Method of Lagrange Multipliers

Christos Tsanas, Erling H. Stenby, Wei Yan

PII: S0009-2509(17)30547-X
DOI: http://dx.doi.org/10.1016/j.ces.2017.08.033
Reference: CES 13776

To appear in: *Chemical Engineering Science*

Received Date: 10 January 2017
Accepted Date: 30 August 2017

Please cite this article as: C. Tsanas, E.H. Stenby, W. Yan, Calculation of Simultaneous Chemical and Phase Equilibrium by the Method of Lagrange Multipliers, *Chemical Engineering Science* (2017), doi: http://dx.doi.org/10.1016/j.ces.2017.08.033

Calculation of Simultaneous Chemical and Phase Equilibrium by the Method of Lagrange Multipliers

Christos Tsanas, Erling H. Stenby, Wei Yan*

Center for Energy Resources Engineering (CERE), Department of Chemistry, Technical University of Denmark, 2800 Kongens Lyngby, Denmark

Abstract

The purpose of this work is to develop a general, reliable and efficient algorithm, which is able to deal with multiple reactions in multiphase systems. We selected the method of Lagrange multipliers to minimize the Gibbs energy of the system, under material balance constraints. Lagrange multipliers and phase amounts are the independent variables, whose initialization is performed by solving a subset of the working equations. This initialization is the unconstrained minimization of a convex function and it is bound to converge. The whole solution procedure employs a nested loop with Newton iteration in the inner loop and non-ideality updated in the outer loop, thus giving an overall linear convergence rate. Stability analysis is used to introduce additional phases sequentially so as to obtain the final multiphase solution. The procedure was successfully tested on vapor-liquid equilibrium (VLE) and vapor-liquid-liquid equilibrium (VLLE) of reaction systems.

Keywords: algorithm, chemical equilibrium, phase equilibrium, heterogeneous synthesis

1. Introduction

Simultaneous chemical and phase equilibrium (CPE) calculations are vital for chemical engineering research and simulations. Even when a process can-

*Corresponding author
Email address: weya@kemi.dtu.dk (Wei Yan)

not reach equilibrium conditions due to kinetic obstructions, CPE calculations provide a thermodynamic limit as reference. Such calculations usually apply in reactive distillation, where the reactions allow separation of desired products or isomers, as well as elimination of azeotropes. Moreover, CPE calculations are needed in heterogeneous organic synthesis, when there are more than one reaction phases. Other applications include weak electrolyte equilibrium in geochemistry and fuels/chemicals from renewable feedstocks.

One of the oldest algorithms for CPE calculations was published by Brinkley (1947), using a nested-loop scheme. Activity coefficients are constant in the inner loop and updated in the outer loop. White et al. (1958) developed an efficient algorithm for ideal mixtures, known as the RAND algorithm, which was generalized for non-ideal multiphase systems by Greiner (1991). Smith and Missen (1982) made a systematic categorization of CPE calculation procedures. According to them, there are two main categories: simultaneous solution of equilibrium equations and Gibbs energy minimization. The second category includes stoichiometric and non-stoichiometric methods, minimizing the Gibbs energy with respect to extents of reactions and using Lagrange multipliers respectively.

The non-stoichiometric problem was thoroughly explained by Zeleznik and Gordon (1968), along with perturbation calculations to initialize computations for challenging systems. Gautam and Wareck (1986) provide a complete set of different reactive flash specifications. Gautam and Seider (1979a,b,c), and White and Seider (1981) published a detailed description of CPE and additional aspects, such as stability analysis or inclusion of electrolytes. Michelsen (1989) introduced an algorithm for ideal mixtures, suggesting implementation of successive substitution in a nested-loop procedure for non-ideal mixtures. Phoenix and Heidemann (1998) developed a stoichiometric and a non-stoichiometric algorithm, starting with a number of phases and combining those of same composition and density during convergence. Barbosa and Doherty (1988), and Ung and Doherty (1995a,b,c,d,e), studied reaction systems, identifying reactive azeotropes and presented a set of transformed composition variables, widely

used by a number of authors in later publications. Pérez Cisneros et al. (1997), with different transformations from those of Barbosa, Doherty and Ung, stressed the dependence of solutions on model parameters.

McDonald and Floudas (1995, 1997), and Floudas and Visweswaran (1990) worked on global optimization methods. Jalali-Farahani and Seader (2000), and Jalali et al. (2008) implemented the homotopy continuation method, mentioning its potential to find all the solutions. Wasylkiewicz and Ung (2000) suggested a method to track all stationary points of the Gibbs energy minimization. Bonilla-Petriciolet et al. (2006, 2011), and Bonilla-Petriciolet and Segovia-Hernández (2010) focused on global optimization using stochastic methods, such as simulated annealing or the firefly algorithm. An alternative approach was presented by Moodley et al. (2015), where the stochastic method simulates the herding behavior of the krill crustacean.

In our work, we have extended the method presented by Michelsen (1989) to non-ideal mixtures and extensively applied it to phase equilibrium of reaction systems. A similar description is outlined in Michelsen and Mollerup (2007) for a single-phase system. Overall, it is a non-stoichiometric algorithm with Lagrange multipliers and phase amounts as independent variables. The minimization equations are solved with Newton's method. Proper initialization of the variables has proven to overcome the problem of divergence. First, one-phase system is assumed and the algorithm is implemented until full convergence. Stability analysis is subsequently utilized to judge, if the addition of a new phase is necessary. The set of phases that is deemed stable, is the final solution. The method was applied to ideal and non-ideal vapor-liquid equilibrium (VLE) and vapor-liquid-liquid equilibrium (VLLE) of reaction systems. Possible applications of interest include heterogeneous organic synthesis and separation, where it is sought to optimize the yields of desired products.

2. Method

2.1. Minimization of Gibbs energy

A multiphase reaction system is at equilibrium, when, under constant temperature and pressure, the Gibbs energy attains its global minimum. Mole numbers of components must satisfy two types of constraints:

- material balance: mass is conserved
- non-negativity: only non-negative mole numbers have physical meaning

Due to chemical reactions, system components are not independent. Provided that there are no additional stoichiometric constraints and we choose a set of linearly independent reactions, the Gibbs phase rule has the form (Rao, 1985):

$$F = N_C - N_R - N_P + 2 \tag{1}$$

where F is the number of degrees of freedom, N_C the number of components, N_R the number of linearly independent chemical reactions and N_P the number of phases. As a result, $N_E = N_C - N_R$ independent entities have to be defined as a basis to describe the system. These entities are called elements and they can be single chemical elements or groups of atoms. The material balance in reaction systems is expressed in terms of elements. Isomers, although share the same chemical composition, must be "composed" by separate elements.

Gibbs energy constrained minimization is concisely formulated as:

$$\begin{aligned} &\min_{\mathbf{n}} G(T,p,\mathbf{n}) = \min_{n_{ik}} \sum_{k=1}^{N_P}\sum_{i=1}^{N_C} n_{ik}\mu_{ik}(T,p,\mathbf{n}_k) \\ \text{s.t.} \quad &\sum_{k=1}^{N_P}\sum_{i=1}^{N_C} A_{ji} n_{ik} = b_j, \quad j = 1,...,N_E \\ &n_{ik} \geq 0, \quad i = 1,...,N_C \qquad k = 1,...,N_P \end{aligned} \tag{2}$$

where G is the Gibbs energy, T the temperature, p the pressure, n_{ik} and μ_{ik} the mole numbers and chemical potential of component i in phase k, $\mathbf{n}_k$ the

components abundance vector in phase k, A_{ji} the number of element j in component i and b_j the total mole numbers of element j. The material balance in the matrix-vector form is:

$$\mathbf{A}\sum_{k=1}^{N_P}\mathbf{n}_k = \mathbf{b} \tag{3}$$

where $\mathbf{A}$ is the formula matrix and $\mathbf{b}$ the element abundance vector. The latter can be found from the single-phase feed mole numbers, $\mathbf{n}_F$:

$$\mathbf{b} = \mathbf{A}\mathbf{n}_F \tag{4}$$

Chemical potential is calculated from:

$$\mu_{ik} = \mu_{ik}^{\circ} + RT\ln\frac{\hat{f}_{ik}}{f_{ik}^{\circ}} \tag{5}$$

where μ_{ik}° is the reference state chemical potential of component i in phase k, R the gas constant, $\hat{f}_{ik}$ the fugacity of component i in phase k and f_{ik}° the reference state fugacity of component i in phase k.

If the same EoS is used for all phases, the ideal gas reference state is selected at the temperature of the system: $\mu_{ik}^{\circ} = \mu_i^*(T, p^*)$ and $f_{ik}^{\circ} = p^*$, where p^* is usually 1 atm or 1 bar. If an activity coefficient model is used for liquid phases, the pure component reference state is selected for those phases at the temperature and pressure of the system: $\mu_{ik}^{\circ} = \mu_{ik}^{\text{pure}}(T, p)$ and $f_{ik}^{\circ} = f_{ik}(T, p)$. The subscript k is used in f_{ik} only to differentiate vapor and liquid pure component fugacities. It is possible to change between the two reference states:

$$\mu_i^* - \mu_{ik}^{\text{pure}} = RT\ln\frac{p^*}{f_{ik}} \tag{6}$$

Fugacities are calculated from an EoS by:

$$\hat{f}_{ik} = x_{ik}\hat{\phi}_{ik}p \tag{7}$$

where x_{ik} is the mole fraction of component i in phase k and $\hat{\phi}_{ik}$ the fugacity coefficient of component i in phase k. For a liquid phase described by an activity

coefficient model, fugacities are calculated by:

$$\hat{f}_{ik} = x_{ik}\gamma_{ik}f_{ik} \tag{8}$$

where γ_{ik} is the activity coefficient of component i in liquid phase k. An equivalent fugacity coefficient is given by:

$$\hat{\phi}_{ik} = \frac{\gamma_{ik}f_{ik}}{p} \tag{9}$$

At low pressures, for a liquid:

$$f_{ik} = p_i^s \tag{10}$$

where p_i^s is the vapor pressure of component i. It must be clarified that ideal vapor phases behave like ideal gases ($\hat{\phi} = 1$), while ideal liquid phases behave like ideal solutions ($\gamma = 1$).

Reactions between components $\mathcal{A}_i$ can be expressed as:

$$\sum_{i=1}^{N_C} \mathcal{A}_i \nu_{ir} = 0, \quad r = 1, ..., N_R \tag{11}$$

where ν_{ir} is the stoichiometric coefficient of component i in reaction r, positive for products and negative for reactants. With stoichiometric coefficients as its entries, the stoichiometric matrix $\mathbf{N}$ is a complete representation of all the reactions. The product of the formula matrix with the stoichiometric matrix must satisfy:

$$\mathbf{AN} = \mathbf{0} \tag{12}$$

Temperature is constant, hence the Gibbs energy has the same minimum as the reduced Gibbs energy, $G/(RT)$. The Lagrangian of the latter is:

$$\mathcal{L}(\mathbf{n}, \boldsymbol{\lambda}) = \sum_{k=1}^{N_P}\sum_{i=1}^{N_C} \frac{n_{ik}\mu_{ik}}{RT} - \sum_{j=1}^{N_E} \lambda_j \left(\sum_{k=1}^{N_P}\sum_{i=1}^{N_C} A_{ji} n_{ik} - b_j \right) \tag{13}$$

where λ_j is the Lagrange multiplier of element j. The solution is a stationary point of the Lagrangian, satisfying:

$$\frac{\partial \mathcal{L}}{\partial n_{ik}} = \frac{\mu_{ik}}{RT} - \sum_{j=1}^{N_E} A_{ji}\lambda_j = 0, \quad i = 1, ..., N_C \qquad k = 1, ..., N_P \tag{14}$$

$$\frac{\partial \mathcal{L}}{\partial \lambda_j} = -\sum_{k=1}^{N_P}\sum_{i=1}^{N_C} A_{ji} n_{ik} + b_j = 0, \quad j = 1, ..., N_E \tag{15}$$

We must mention that this point is a saddle of the Lagrangian. The purpose is not to minimize the Lagrangian, but the reduced Gibbs energy. Instead of solving this set of equations, we introduce the mole fractions and the phase amounts in Eq. 15:

$$F_j^A = \sum_{k=1}^{N_P} n_{t,k} \sum_{i=1}^{N_C} A_{ji} x_{ik} - b_j = 0, \quad j = 1, ..., N_E \tag{16}$$

Mole fractions in each phase must also satisfy:

$$F_k^B = \sum_{i=1}^{N_C} x_{ik} - 1 = 0, \quad k = 1, ..., N_P \tag{17}$$

From Eq. 5 and 14, the mole fraction can be expressed as a function of the Lagrange multipliers:

$$\ln x_{ik} = \sum_{j=1}^{N_E} A_{ji}\lambda_j - \frac{\mu_{ik}^\circ}{RT} - \ln \frac{\hat{\phi}_{ik} p}{f_{ik}^\circ} \tag{18}$$

The working equations of the procedure are given by Eq. 16 and 17. The independent variables at equilibrium, $\boldsymbol{\lambda}$ and $\mathbf{n}_t$, are roots of the function $\mathbf{F}$:

$$\mathbf{F}(\boldsymbol{\lambda}, \mathbf{n}_t) = \begin{bmatrix} \mathbf{F}^A \\ \mathbf{F}^B \end{bmatrix} \tag{19}$$

To find the Jacobian of $\mathbf{F}$, derivatives of x_{ik} are required. Whenever we use the Jacobian in calculations, we assume that the fugacity coefficients are constant. Therefore:

$$\frac{\partial x_{ik}}{\partial \lambda_q} = A_{qi} x_{ik}, \quad q = 1, ..., N_E \tag{20}$$

and:

$$\frac{\partial x_{ik}}{\partial n_{t,q}} = 0, \quad q = 1, ..., N_P \tag{21}$$

Finally, the Jacobian matrix of function $\mathbf{F}$ has the form:

$$\mathbf{J}(\boldsymbol{\lambda}, \mathbf{n}_t) = \begin{bmatrix} \mathbf{J}^A & \mathbf{J}^B \\ \mathbf{J}^C & \mathbf{J}^D \end{bmatrix} \tag{22}$$

where:

$$J^A_{jq} = \frac{\partial F^A_j}{\partial \lambda_q} = \sum_{k=1}^{N_P} n_{t,k} \sum_{i=1}^{N_C} A_{ji} A_{qi} x_{ik}, \quad j = 1, ..., N_E \qquad q = 1, ..., N_E \tag{23}$$

$$J^B_{jq} = \frac{\partial F^A_j}{\partial n_{t,q}} = \sum_{i=1}^{N_C} A_{ji} x_{iq}, \quad j = 1, ..., N_E \qquad q = 1, ..., N_P \tag{24}$$

$$J^C_{kq} = \frac{\partial F^B_k}{\partial \lambda_q} = \sum_{i=1}^{N_C} A_{qi} x_{ik} = J^B_{qk}, \quad k = 1, ..., N_P \qquad q = 1, ..., N_E \tag{25}$$

$$J^D_{kq} = \frac{\partial F^B_k}{\partial n_{t,q}} = 0, \quad k = 1, ..., N_P \qquad q = 1, ..., N_P \tag{26}$$

or

$$\mathbf{J}(\boldsymbol{\lambda}, \mathbf{n}_t) = \begin{bmatrix} \mathbf{J}^A & \mathbf{J}^B \\ (\mathbf{J}^B)^{\mathrm{T}} & \mathbf{0} \end{bmatrix} \tag{27}$$

The solution of $\mathbf{F}$ is determined iteratively with the Newton's method:

$$\mathbf{J} \begin{bmatrix} \Delta\boldsymbol{\lambda} \\ \Delta\mathbf{n}_t \end{bmatrix} = -\mathbf{F} \tag{28}$$

A nested-loop scheme is employed: in the inner loop we keep constant the values of fugacity or activity coefficients. When the estimate of Eq. 28 converges, we update all non-ideality quantities in the outer loop. The dimensions of the system in the inner loop is $N_E + N_P$. The original working equations (Eq.

14 and 15) require determining a total of $N_C N_P + N_E$ variables, whereas the nested-loop scheme uses $(N_C - 1)N_P$ fewer variables. According to Eq. 14, a relationship can be found between the minimum Gibbs energy and the Lagrange multipliers:

$$\begin{aligned}\frac{G_{\min}}{RT} &= \sum_{k=1}^{N_P}\sum_{i=1}^{N_C}\frac{n_{ik}\mu_{ik}}{RT} = \sum_{k=1}^{N_P}\sum_{i=1}^{N_C} n_{ik}\sum_{j=1}^{N_E} A_{ji}\lambda_j = \\ &= \sum_{j=1}^{N_E}\lambda_j\sum_{k=1}^{N_P}\sum_{i=1}^{N_C} A_{ji}n_{ik} = \sum_{j=1}^{N_E} b_j\lambda_j\end{aligned} \tag{29}$$

Eq. 29 shows that the minimum Gibbs energy is a homogeneous function of degree one in the mole numbers of the elements b_j, therefore:

$$\left(\frac{\partial G_{\min}}{\partial b_j}\right)_{T,p,b_{q\neq j}} = RT\lambda_j \tag{30}$$

In other words, the Lagrange multipliers represent the reduced chemical potential of the elements at equilibrium.

2.2. Initialization

To initialize calculations, usually a linear programming problem is solved for non-zero mole numbers of N_E components (Michelsen and Mollerup, 2007). From this solution we can determine estimates of $\boldsymbol{\lambda}$ and $\mathbf{n}_t$. Disadvantages associated with this method are, except degenerate cases, the poor estimation of small concentrations or the possibility that we find a solution with less than N_E components present. In this case, there is not enough information to determine $\boldsymbol{\lambda}$ (Michelsen and Mollerup, 2007).

To avoid solving this problem, we estimate the phase amounts and determine the Lagrange multipliers from an unconstrained minimization problem. In general, it is easier to decide on a reasonable estimate for $\mathbf{n}_t$ rather than $\boldsymbol{\lambda}$ at equilibrium. We assume that the mole numbers of a single phase will be between a minimum and a maximum value, due to reactions. In this work, the initial guess for n_t was selected as the average of these two values. Although generalization for a multiphase system is not addressed here, initial estimates of

phase amounts were found less critical for convergence. Once the phase amounts are initialized, they are kept constant and the following function is defined:

$$Q(\boldsymbol{\lambda}) = \sum_{k=1}^{N_P} n_{t,k} \left(\sum_{i=1}^{N_C} x_{ik} - 1 \right) - \sum_{j=1}^{N_E} \lambda_j b_j \tag{31}$$

The unconstrained minimization of function Q provides initial estimates of the Lagrange multipliers. This involves the solution of:

$$\nabla^2 Q \Delta\boldsymbol{\lambda} = -\nabla Q \tag{32}$$

or, according to Eq. 16 and 23:

$$\mathbf{J}^A \Delta\boldsymbol{\lambda} = -\mathbf{F}^A \tag{33}$$

The matrix-vector form of Eq. 23 is:

$$\mathbf{J}^A = \mathbf{A}\, \mathrm{diag} \left(\sum_{k=1}^{N_P} \mathbf{n}_k \right) \mathbf{A}^{\mathrm{T}} \tag{34}$$

The entries of the diagonal matrix are the total mole numbers of each component, which are positive. Consequently, the diagonal matrix is positive definite. Since matrix $\mathbf{A}$ has full rank, matrix $\mathbf{J}^A$ is positive definite as well. Function Q is convex and we will ultimately find its unique minimizer. The Lagrange multipliers we calculated and the phase amounts we guessed are initial estimates for the full Newton's method in Eq. 28.

2.3. Stability analysis

We must perform stability analysis to verify that no additional phase can lower the current Gibbs energy of the system. The method used was presented by Michelsen (1982) and later in Michelsen and Mollerup (2007): a phase with composition $\mathbf{z}$ is unstable when there is composition $\mathbf{w}$, for which the tangent plane distance $TPD(\mathbf{w})$ is negative:

$$TPD(\mathbf{w}) = \sum_{i=1}^{N_C} w_i \left[\mu_i(\mathbf{w}) - \mu_i(\mathbf{z}) \right] < 0 \tag{35}$$

Negative values of TPD can be identified through determination of its minima (Michelsen, 1982) and a phase split occurs if a negative TPD is found during the search. Stability analysis for multiphase calculations is essentially the same as for a two-phase system. Any phase of the converged solution can be used to test the overall stability. However, special care needs to be taken for the initial estimates in multiphase calculation (Michelsen, 1982; Michelsen and Mollerup, 2007).

2.4. Assignment of reference state chemical potential

The reference state chemical potential is needed to calculate mole fractions from Eq. 18. It can be found in tables for specific T and p. Although necessary, this information is not always available. Instead, chemical equilibrium constants are more frequently reported:

$$K_{rk}^{\mathrm{eq}} = \exp\left(-\frac{\Delta_r G_{rk}^{\circ}}{RT}\right) = \exp\left(-\sum_{i=1}^{N_C}\frac{\nu_{ir}\mu_{ik}^{\circ}}{RT}\right) \tag{36}$$

where K_{rk}^{eq} is the chemical equilibrium constant of reaction r in phase k and $\Delta_r G_{rk}^{\circ}$ the reference state Gibbs energy of reaction r in phase k, which can also be calculated based on the Gibss energy of formation or Gibbs energy of combustion.

In total N_C reference state chemical potentials are missing from phase k, but there are only N_R chemical equilibrium constants. Absolute values of μ_{ik}° do not matter for the calculations, as long as they satisfy Eq. 36. In place of the real reference state chemical potential, we "decompose" the chemical equilibrium constants into fictitious, yet consistent, values: N_R reference components are selected, that participate in one reaction at least (no inerts) and we assign:

$$\mu_{ik}^{\circ} = \begin{cases} \hat{\mu}_{ik}, & i \in \text{reference components} \\ 0, & i \notin \text{reference components} \end{cases} \tag{37}$$

The following system is solved for $\hat{\boldsymbol{\mu}}_k/(RT)$:

$$\frac{1}{RT}\hat{\mathbf{N}}^{\mathrm{T}}\hat{\boldsymbol{\mu}}_k = \begin{bmatrix} -\ln K_{1k}^{\mathrm{eq}} \\ . \\ . \\ . \\ -\ln K_{rk}^{\mathrm{eq}} \end{bmatrix} \tag{38}$$

where $\hat{\mathbf{N}}$ is the stoichiometric matrix of the N_R reference components we chose. When all phases share the same reference state, then $\mu_{ik}^{\circ} = \mu_{iq}^{\circ}\big|_{q\neq k}$ for all components. Otherwise, Eq. 6 must be used.

3. Results and discussion

In this work, Q function (Eq. 31) is minimized assuming a single ideal phase. Afterwards, stability analysis provides the necessary composition estimates, when an additional phase must be considered. Starting values for the Lagrange multipliers in the new phase set are taken from the previous solution and $n_{t,\text{new phase}} = 0$. The procedure stops when the maximum error in the independent variables ($\boldsymbol{\lambda}$ and $\mathbf{n}_t$) is less than 10^{-10}. The error at iteration $q \geq 1$ is calculated as:

$$\text{error}^{(q)} = \sqrt{\sum_{j=1}^{N_E}\left[\lambda_j^{(q)} - \lambda_j^{(q-1)}\right]^2 + \sum_{k=1}^{N_P}\left[n_{t,k}^{(q)} - n_{t,k}^{(q-1)}\right]^2} \tag{39}$$

Figure 1 summarizes the suggested procedure for solving CPE involving multiple phases and multiple reactions. It should be noted that this method is intended to provide a general and safe solution. Therefore, calculations start from a single phase and additional phases are introduced in a step-wise manner, one at a time. It is possible to start calculations from more than one phases. Although more risky, this might save time in actual calculation. Our trials have shown that the algorithm converges for most tested cases, even if initially $N_P > 1$. Nevertheless, this is not the focus of this work.

Table 1: Component and element numbering for the systems examined.

System		1	2	3	4	5	6	7
Formaldehyde/ water	Component	Formaldehyde	Water	Methylene glycol	Oxydimethanol			
	Element	CH_2O	H_2O					
Xylene separation	Component	Di-*tert*-butylbenzene	*m*-Xylene	*tert*-Butyl-*m*-xylene	*tert*-Butylbenzene	Benzene	*p*-Xylene	
	Element	C_6H_6	C_4H_8	C_8H_{10}	C_8H_{10} (inert)			
MTBE synthesis	Component	Isobutene	Methanol	*n*-Butane	MTBE			
	Element	C_4H_8	CH_4O	C_4H_{10} (inert)				
Acetic acid/ethanol esterification	Component	Acetic acid	Ethanol	Water	Ethyl acetate			
	Element	C_2H_2O	C_2H_6O	H_2O				
Cyclohexane synthesis	Component	Benzene	Hydrogen	Cyclohexane				
	Element	C_6H_6	H_2					
Methanol synthesis	Component	Carbon monoxide	Carbon dioxide	Hydrogen	Water	Methanol	Methane	Octadecane
	Element	CO	O	H_2	CH_4 (inert)	$C_{18}H_{38}$ (inert)		

For simplicity, components and elements are numbered in each mixture. Table 1 illustrates the identity of components and the chemical composition of elements in the systems included in this work. Results reported are mole fractions x_{ik}, phase amounts $n_{t,k}$ and phase fractions β_k, given by:

$$\beta_k = \frac{n_{t,k}}{\sum_{q=1}^{N_P} n_{t,q}} \tag{40}$$

The main CPE solver as well as thermodynamic routines were all coded in FORTRAN using the compiler from Intel® Parallel Studio XE 2015. In the current implementation we use functions provided by Intel® MKL libraries (LAPACK). Function `DSYTRF` to factorize a symmetric matrix (LDL decomposition) and `DSYTRS` to solve the system. Other Cholesky decomposition routines have similar performance. EoS or activity coefficient models are implemented in a modular way, to avoid making the problem "fugacity-expression" dependent. The input of the routines is temperature, pressure and component mole numbers of a phase to obtain: from an activity coefficient model directly the activity coeffiients and from an EoS, after solving numercally for volume, the fugacity coefficients.

3.1. System based on the chemistry of formaldehyde/water

Maurer (1986) presented a set of reactions occuring in aqueous solutions of formaldehyde. Here, similar to Ung and Doherty (1995e), only formation

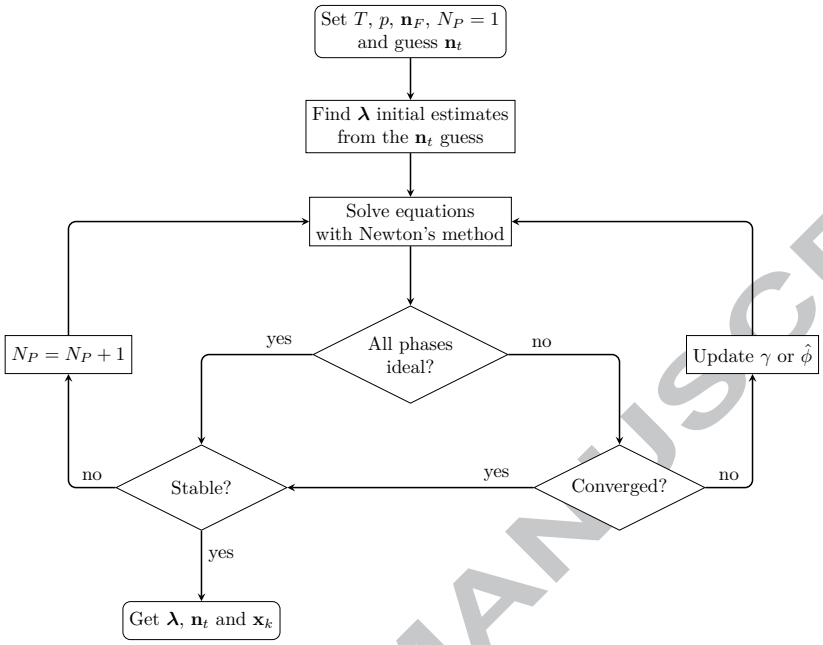


Figure 1: Flowchart of the reported algorithm.

of methylene glycol and oxydimethanol (dimer in polyoxymethylene polymerization) are considered for the calculations. Formaldehyde reacts with water to produce methylene glycol, which subsequently produces oxydimethanol in a condensation dimerization:

$$\mathrm{CH_2O + H_2O \rightleftharpoons CH_4O_2} \tag{41}$$

$$\mathrm{2CH_4O_2 \rightleftharpoons C_2H_6O_3 + H_2O} \tag{42}$$

The number of elements is $N_E = N_C - N_R = 4 - 2 = 2$. The formula matrix and stoichiometric matrix of the system are given by:

$$\mathbf{A} = \begin{bmatrix} 1 & 0 & 1 & 2 \\ 0 & 1 & 1 & 1 \end{bmatrix} \qquad \mathbf{N} = \begin{bmatrix} -1 & -1 & 1 & 0 \\ 0 & 1 & -2 & 1 \end{bmatrix}^{\mathrm{T}} \tag{43}$$

Vapor and liquid phases are considered ideal as in Ung and Doherty (1995e), unlike in Maurer (1986), who used the UNIFAC activity coefficient model (Fre-

denslund et al., 1975) for the liquid phase. Chemical equilibrium constants and vapor pressure expressions were taken from Maurer (1986). Oxydimethanol is considered non-volatile and consequently its concentration in the vapor phase is zero. Both phases are ideal and as a result there are no non-reactive azeotropes. Ung and Doherty (1995e) showed that there are no reactive azeotropes either. Equilibrium $T - y - x$ diagrams at 1 atm for all system components are presented in Figure 2. As mentioned in Ung and Doherty (1995e), reactions do not allow the concentration of every component to span the full range [0,1]. For instance, it can be seen from Eq. 42, that a pure methylene glycol solution does not exist, because pairs of these molecules produce dimers through condensation. Maximum methylene glycol in the vapor phase is less than 0.1% at 315.98 K. Maximum concentrations in the liquid phase are $x_3 = 0.24$ at 304.07 K for methylene glycol and $x_4 = 0.60$ at 285.02 K for oxydimethanol.

3.2. Xylene separation

Saito et al. (1971) examined the possibility of separating *m*- and *p*-xylene. Normal distillation is not applicable, since isomers have close boiling points and crystallization has certain limitations. They chose reactive distillation, taking advantage of the following reactions:

$$C_{14}H_{22} + m\text{-}C_8H_{10} \rightleftharpoons C_{12}H_{18} + C_{10}H_{14} \tag{44}$$

$$C_{10}H_{14} + m\text{-}C_8H_{10} \rightleftharpoons C_{12}H_{18} + C_6H_6 \tag{45}$$

where di-*tert*-butylbenzene reacts with *m*-xylene to produce *tert*-butyl-*m*-xylene and *tert*-butylbenzene, the latter reacting at the same time with *m*-xylene to produce *tert*-butyl-*m*-xylene and benzene. In this reaction system, *p*-xylene is an inert. The number of elements is $N_E = N_C - N_R = 6 - 2 = 4$. The formula

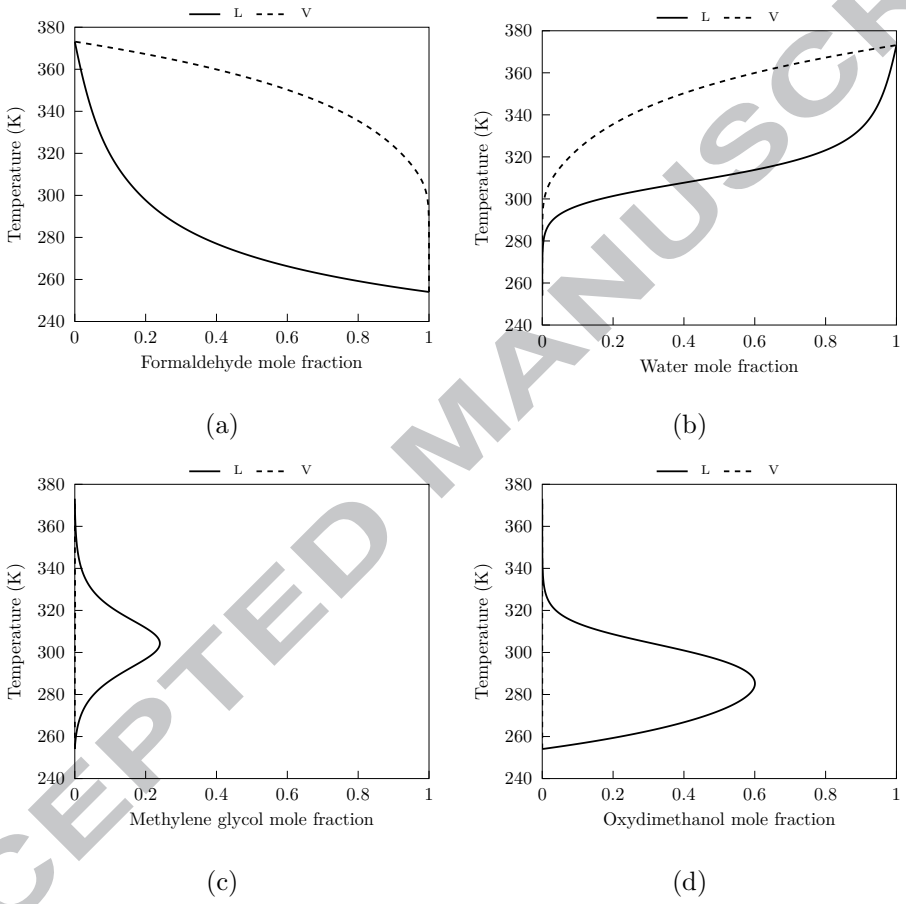


Figure 2: Equilibrium T-y-x diagrams for formaldehyde (a), water (b), methylene glycol (c) and oxydimethanol (d) at 1 atm.

Table 2: Mole fractions in xylene separation at the bubble point of 44 mmHg.

Component	Feed	Our work – 336.54 K		Saito et al. (1971) – 331.15 K
		Vapor	Liquid	Vapor
Di-*tert*-butylbenzene	0.29	0.01	0.29	0.02
m-Xylene	0.08	0.10	0.08	0.14
tert-Butyl-*m*-xylene	0.07	0.01	0.07	0.01
tert-Butylbenzene	0.19	0.08	0.19	0.11
Benzene	0.03	0.34	0.03	0.22
p-Xylene	0.34	0.47	0.34	0.50

matrix and stoichiometric matrix of the system are given by:

$$\mathbf{A} = \begin{bmatrix} 1 & 0 & 0 & 1 & 1 & 0 \\ 2 & 0 & 1 & 1 & 0 & 0 \\ 0 & 1 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \qquad \mathbf{N} = \begin{bmatrix} -1 & -1 & 1 & 1 & 0 & 0 \\ 0 & -1 & 1 & -1 & 1 & 0 \end{bmatrix}^{\mathrm{T}} \tag{46}$$

Vapor and liquid phases are ideal. Chemical equilibrium constants and vapor pressure expressions were taken from Saito et al. (1971). The authors determined experimentally compositions at different plates in two distillation columns: lower pressure alkylation column of *m*-xylene and higher pressure recovery column of *m*-xylene and alkylating reagent. Bubble point calculations are performed for the 1st plate/condenser of the column and compared with the experimental compositions (Saito et al., 1971) in Tables 2 and 3. At both temperatures, highest deviations are noted for benzene. In Figure 3, for the same feed compositions, we present the temperature range of the 2-phase system, as well as the mole fractions of each component. Most mole fractions curves exhibit monotonic behavior. Although xylene isomer compositions might have maxima in the two different pressures and phases, *p*-xylene shows the clearest maximum at 347.52 K and 44 mmHg with a vapor phase composition of $y_6 = 0.557$.

Table 3: Mole fractions in xylene separation at the bubble point of 86 mmHg.

Component	Feed	Our work – 324.40 K		Saito et al. (1971) – 323.15 K
		Vapor	Liquid	Vapor
Di-*tert*-butylbenzene	0.09	0.00	0.07	0.00
m-Xylene	0.35	0.13	0.34	0.29
tert-Butyl-*m*-xylene	0.04	0.00	0.05	0.00
tert-Butylbenzene	0.21	0.03	0.24	0.05
Benzene	0.25	0.82	0.24	0.59
p-Xylene	0.06	0.02	0.06	0.07

3.3. MTBE synthesis

Ung and Doherty (1995e) studied the phase behavior of methyl-*tert*-butyl ether (MTBE) synthesis from isobutene and methanol in the presence of *n*-butane as an inert:

$$C_4H_8 + CH_4O \rightleftharpoons C_5H_{12}O \tag{47}$$

The number of elements is $N_E = N_C - N_R = 4 - 1 = 3$. The formula matrix and stoichiometric matrix of the system are given by:

$$\mathbf{A} = \begin{bmatrix} 1 & 0 & 0 & 1 \\ 0 & 1 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix} \qquad \mathbf{N} = \begin{bmatrix} -1 & -1 & 0 & 1 \end{bmatrix}^{\mathrm{T}} \tag{48}$$

Vapor phase is considered ideal and liquid phase is described by the Wilson activity coefficient model (Wilson, 1964). The chemical equilibrium constant, vapor pressure expressions and parameters for the Wilson model were taken from Ung and Doherty (1995e). At a reactive azeotrope, Ung and Doherty (1995b) proved that mole fractions in the two phases are not necessarily equal. Instead, they introduce a set of transformed composition variables, denoted by capital letters, which simplifies the analysis. According to their new notation, at a reactive azeotrope $X = Y$ for all reference components. For this system,

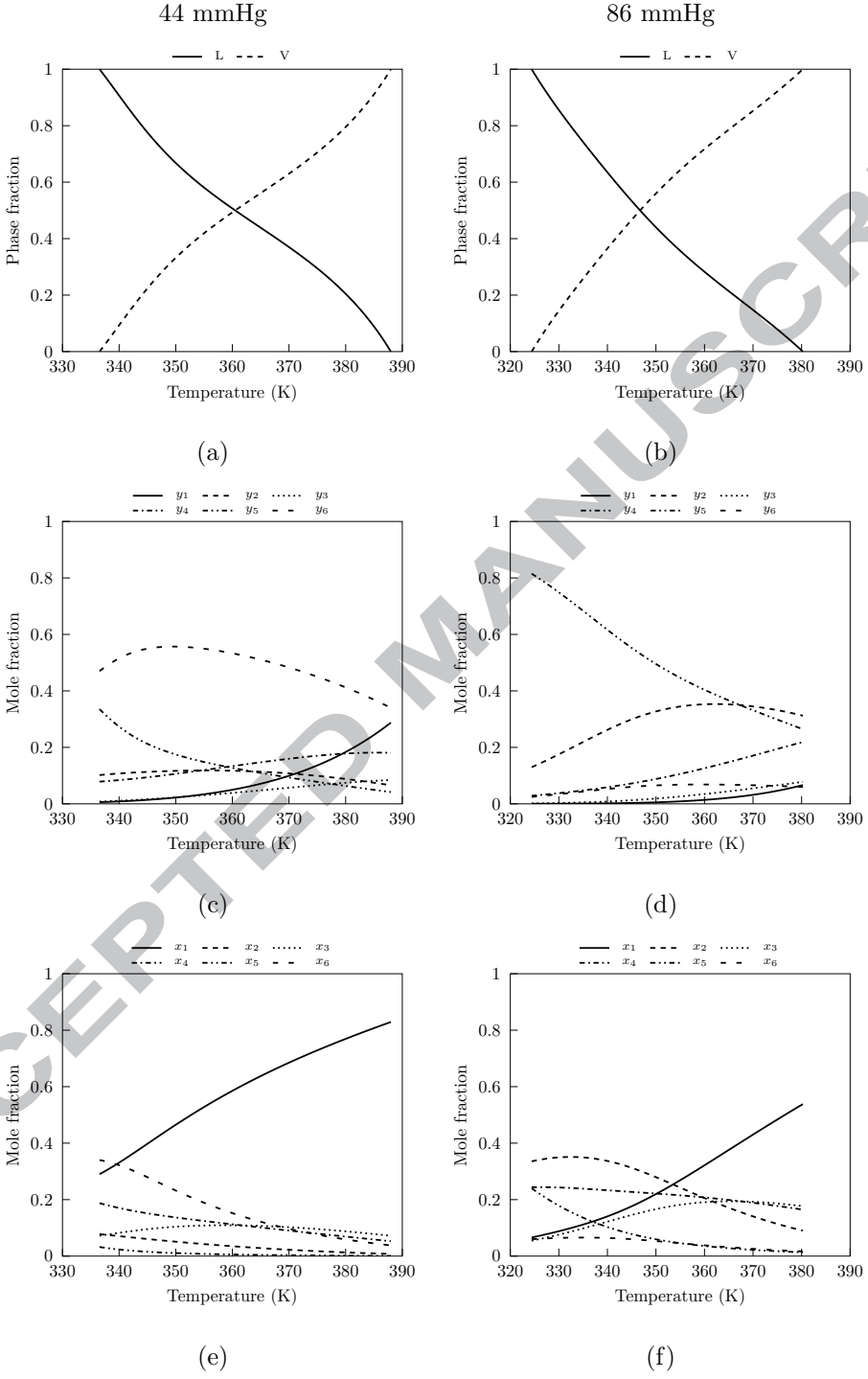


Figure 3: Phase fractions (a, b) and mole fractions (c, d, e, f) in xylene separation for the feeds reported in Tables 2 and 3.

transformed compositions are found by:

$$X_1 = \frac{x_1 + x_4}{1 + x_4} \qquad X_2 = \frac{x_2 + x_4}{1 + x_4} \qquad X_3 = \frac{x_3}{1 + x_4} \tag{49}$$

For the derivation and the implications of transformed variables, the reader is referred to Ung and Doherty (1995b,d). The equilibrium diagrams at 1 atm are presented in Figures 4a and 4b using transformed compositions. The inert was not considered in these calculations. An "intermediate-boiling inflection azeotrope" is identified, or according to Ung and Doherty (1995e), a "pseudo-reactive azeotrope", for being fairly close to the diagonal (Figure 4b). We observed this point at 320.92 K. In Figure 4c, we find that the maximum MTBE concentrations are $y_4 = 0.70$ in the vapor phase at 320.56 K and $x_4 = 0.93$ in the liquid phase at 317.70 K. The absence of the inert allows us to depict all the equilibrium curves in two-dimensional diagrams.

We also examined the inert effect in the following conditions: 300 K and 1 atm with an equimolar feed of reactants (isobutene and methanol, 1 mol each). Different values of mole numbers for the inert were included in this feed and the effects on the overall equilibrium are presented in Figure 5. Phase fractions and mole fractions of all the components are shown, as the inert concentration increases in the feed. The vapor pressure expression constants for n-butane were taken from NIST Chemistry WebBook (Accessed: 19.02.2016). Since the inert is volatile, a vapor phase appears with the addition of approximately 0.36 mol of n-butane, after which the vapor phase fraction increases with n-butane concentration until we obtain 100% vapor. The mole fraction of MTBE (Figure 5e) for a single phase decreases as the moles of the inert in the feed increase. In the two-phase region, the phase compositions of MTBE and n-butane (Figures 5d and 5e) change only slightly. However, the overall mole fraction of MTBE (the total moles of MTBE divided by the total moles of the components in the system) decreases continuously as a result of the dilution by the inert component.

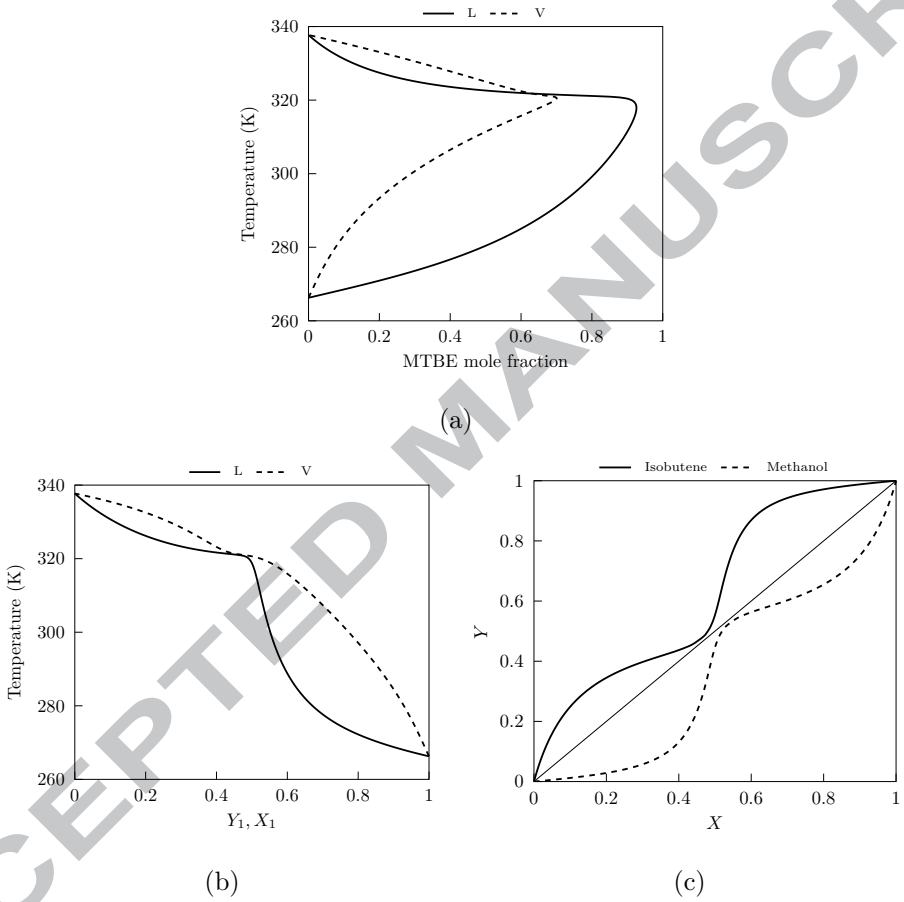


Figure 4: Equilibrium T-y-x diagram for MTBE (a), T-Y-X diagram for isobutene (b) and Y-X diagram for isobutene and methanol (c) in MTBE synthesis at 1 atm.

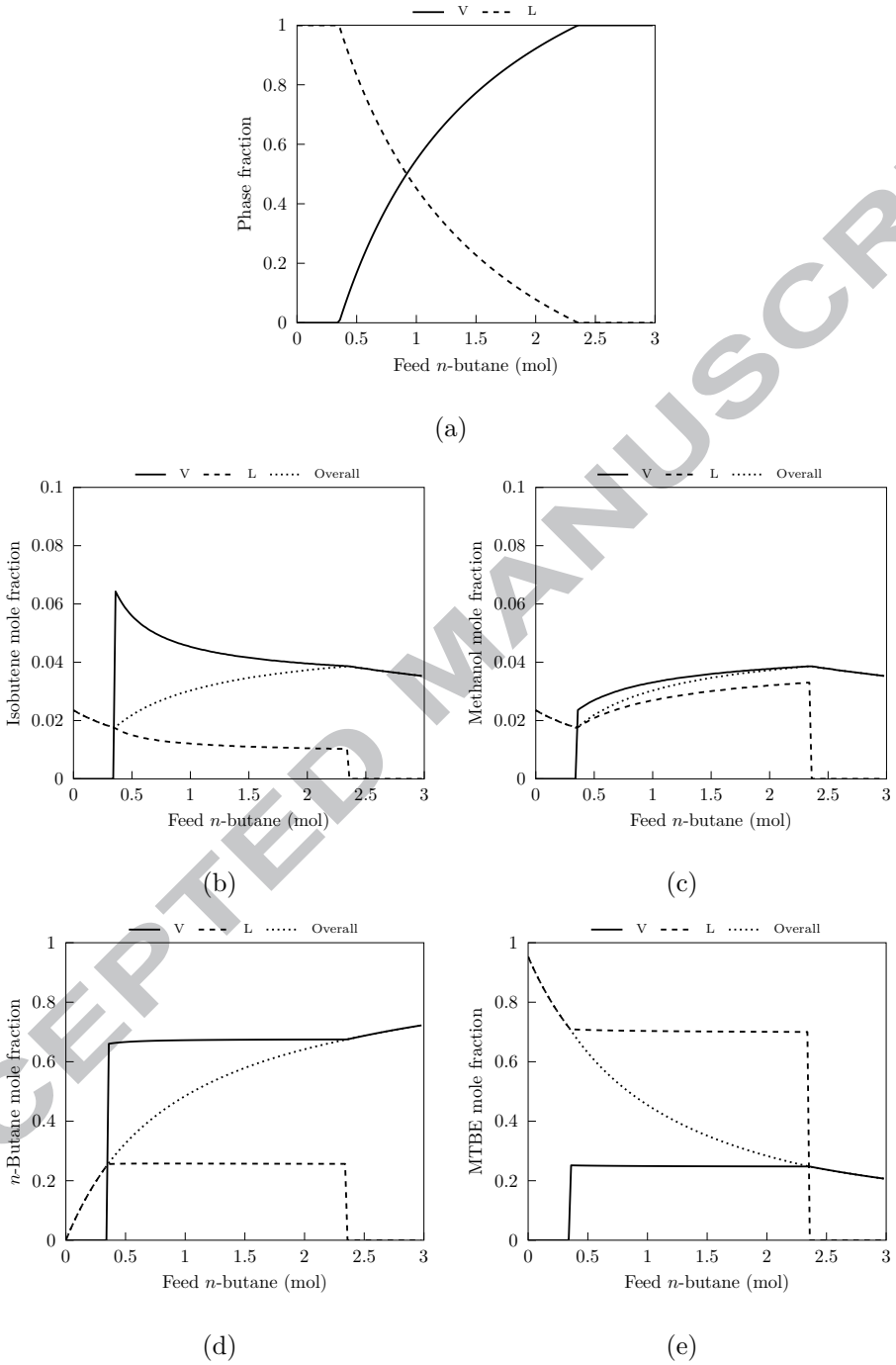


Figure 5: Phase fractions (a), mole fractions of isobutene (b), methanol (c), n-butane (d) and MTBE (e) as a function of n-butane moles in the feed for the MTBE synthesis at 300 K and 1 atm.

3.4. Esterification of acetic acid and ethanol

One of the most studied esterification reactions is between acetic acid and ethanol producing ethyl acetate and water:

$$C_2H_4O_2 + C_2H_6O \rightleftharpoons C_4H_8O_2 + H_2O \tag{50}$$

The number of elements is $N_E = N_C - N_R = 4 - 1 = 3$. The formula matrix and stoichiometric matrix of the system are given by:

$$\mathbf{A} = \begin{bmatrix} 1 & 0 & 0 & 1 \\ 0 & 1 & 0 & 1 \\ 1 & 0 & 1 & 0 \end{bmatrix} \qquad \mathbf{N} = \begin{bmatrix} -1 & -1 & 1 & 1 \end{bmatrix}^{\mathrm{T}} \tag{51}$$

Vapor phase is considered ideal and liquid phase is described by the UNIQUAC activity coefficient model (Abrams and Prausnitz, 1975). The chemical equilibrium constant, vapor pressure expressions and parameters for the UNIQUAC model were taken from Xiao et al. (1989). Castier et al. (1989) studied this system including the competing etherification reaction of ethanol to diethylether as well as the dimerization of acetic acid in the vapor phase. Comparisons are made with the results of Xiao et al. (1989), and Stateva and Wakeham (1997) in Table 4. Larger deviations with Stateva and Wakeham (1997) could be attributed to selecting a different source for the chemical equilibrium constant. In Figure 6, phase boundaries and mole fractions are presented for an equimolar feed of the reactants.

3.5. Cyclohexane synthesis

George et al. (1976) examined the hydrogenation of benzene at high temperature for cyclohexane synthesis:

$$C_6H_6 + 3H_2 \rightleftharpoons C_6H_{12} \tag{52}$$

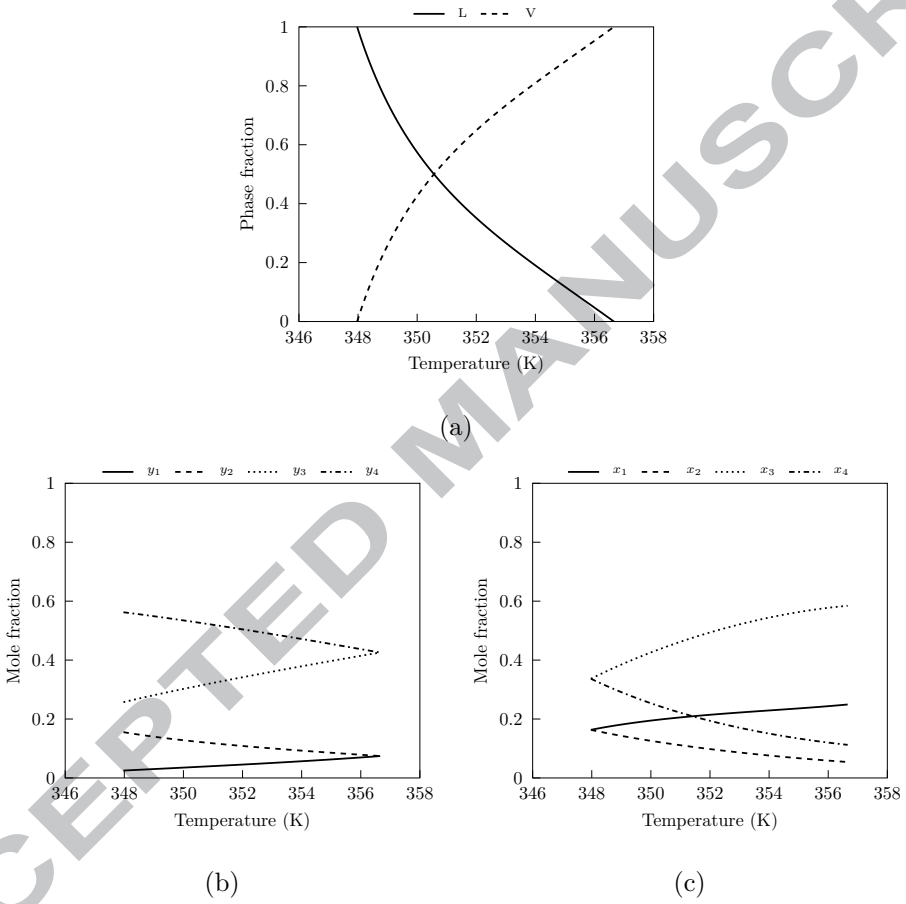


Figure 6: Phase fractions (a) and mole fractions (b, c) in acetic acid/ethanol esterification for an equimolar feed of reactants at 1 atm.

Table 4: Mole fractions, phase amounts and phase fractions in acetic acid/ethanol esterification at 355 K and 1 atm.

Component	Feed	Our work		Stateva and Wakeham (1997)		Xiao et al. (1989)	
		Vapor	Liquid	Vapor	Liquid	Vapor	Liquid
Acetic acid	0.5	0.0629	0.2360	0.0554	0.2243	0.0624	0.2376
Ethanol	0.5	0.0855	0.0670	0.1029	0.0675	0.0862	0.0686
Water	0	0.3970	0.5630	0.3604	0.5537	0.3963	0.5565
Ethyl acetate	0	0.4545	0.1339	0.4813	0.1545	0.4551	0.1373
n_t (mol)	20	17.636	2.364				
β		0.882	0.118	0.767	0.233	0.877	0.123

The number of elements is $N_E = N_C - N_R = 3 - 1 = 2$. The formula matrix and stoichiometric matrix of the system are given by:

$$\mathbf{A} = \begin{bmatrix} 1 & 0 & 1 \\ 0 & 1 & 3 \end{bmatrix} \qquad \mathbf{N} = \begin{bmatrix} -1 & -3 & 1 \end{bmatrix}^{\mathrm{T}} \tag{53}$$

Phase behavior is described by the Peng-Robinson equation of state (Peng and Robinson, 1976) without binary interaction parameters ($k_{ij} = 0$), similar to Burgos-Solórzano et al. (2004). Gibbs energy of formation was taken from George et al. (1976). Calculations are shown in Table 5. Small differences with Burgos-Solórzano et al. (2004) are attributed to selecting a different source for the chemical equilibrium constant. George et al. (1976) assumed that the system obeys the Lewis fugacity rule, underestimating the influence of intermolecular forces, hence predicting larger vapor phase amount.

3.6. Methanol synthesis

Methanol can be synthesized from a mixture containing carbon monoxide, carbon dioxide, hydrogen and water, according to the reactions:

Table 5: Mole fractions, phase amounts and phase fractions in cyclohexane synthesis at 500 K and 30 atm.

Component	Feed	Our work		Burgos-Solórzano et al. (2004)		George et al. (1976)	
		Vapor	Liquid	Vapor	Liquid	Vapor	Liquid
Benzene	0.247	4.45×10^{-6}	5.43×10^{-6}	4.00×10^{-6}	4.92×10^{-6}	3.64×10^{-4}	3.87×10^{-4}
Hydrogen	0.753	0.238	0.0204	0.249	0.0147	0.076	0.0023
Cyclohexane	0	0.762	0.980	0.751	0.985	0.923	0.997
n_t (mol)	4.05	0.132	0.918	0.148	0.902	0.660	0.391
β		0.125	0.875	0.141	0.859	0.628	0.372

$$CO + 2H_2 \rightleftharpoons CH_4O \tag{54}$$

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \tag{55}$$

Methane and octadecane are included as inerts. The number of elements is $N_E = N_C - N_R = 7 - 2 = 5$. The formula matrix and stoichiometric matrix of the system are given by:

$$\mathbf{A} = \begin{bmatrix} 1 & 1 & 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 1 & 2 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \qquad \mathbf{N} = \begin{bmatrix} -1 & 0 & -2 & 0 & 1 & 0 & 0 \\ 1 & -1 & -1 & 1 & 0 & 0 & 0 \end{bmatrix}^{\mathrm{T}} \tag{56}$$

Phase behavior is described by the Soave-Redlich-Kwong equation of state (Soave, 1972) with binary interaction parameters k_{ij} from Castier et al. (1989). Ideal gas chemical potentials at 1 bar (reference state) were taken from Phoenix and Heidemann (1998). In Tables 6 and 7, two different feeds are used to produce methanol, resulting in a 2- and 3-phase system respectively. Results from Stateva and Wakeham (1997), and Castier et al. (1989) are also included for comparison. Introduction of the heavy hydrocarbon results in two immiscible liquid phases along with the vapor phase. For identification purposes, we named

Table 6: Mole fractions, phase amounts and phase fractions in methanol synthesis at 473.15 K and 300 bar.

Component	Feed	Our work		Stateva and Wakeham (1997)		Castier et al. (1989)	
		Vapor	Liquid	Vapor	Liquid	Vapor	Liquid
Carbon monoxide	0.15	6.27×10^{-5}	1.09×10^{-5}	1.33×10^{-5}	traces	6.51×10^{-5}	1.08×10^{-5}
Carbon dioxide	0.08	0.0006	0.0003	traces	traces	0.0005	0.0002
Hydrogen	0.74	0.6597	0.0970	0.6493	0.0948	0.6589	0.0962
Water	0	0.0471	0.2432	0.0464	0.2488	0.0473	0.2436
Methanol	0	0.2045	0.6349	0.2120	0.6371	0.2053	0.6354
Methane	0.3	0.0880	0.0246	0.0923	0.0193	0.0878	0.0246
Octadecane	0	0	0	0	0	0	0
n_t (mol)	100	26.346	27.702			26.421	27.622
β		0.4875	0.5125	0.4968	0.5032	0.4889	0.5111

Table 7: Mole fractions, phase amounts and phase fractions in methanol synthesis at 473.15 K and 101.3 bar.

Component	Feed	Our work			Stateva and Wakeham (1997)			Castier et al. (1989)		
		Vapor	Liquid (aq)	Liquid (org)	Vapor	Liquid (aq)	Liquid (org)	Vapor	Liquid (aq)	Liquid (org)
Carbon monoxide	0.1071	0.0010	7.00×10^{-6}	0.0002	5.63×10^{-8}	1.27×10^{-10}	4.80×10^{-9}	0.0011	6.82×10^{-6}	0.0002
Carbon dioxide	0.0571	0.0548	0.0025	0.0271	7.27×10^{-12}	2.96×10^{-6}	3.18×10^{-12}	0.0534	0.0024	0.0270
Hydrogen	0.5286	0.5741	0.0059	0.1091	0.5328	0.0071	0.0600	0.5731	0.0058	0.1159
Water	0.2143	0.1718	0.7715	0.1104	0.1635	0.7047	0.0070	0.1722	0.7709	0.1116
Methanol	0	0.1426	0.2197	0.2767	0.2274	0.2870	0.1418	0.1441	0.2205	0.2753
Methane	0.0214	0.0544	0.0004	0.0182	0.0752	0.0011	0.0210	0.0546	0.0004	0.0192
Octadecane	0.0715	0.0014	1.18×10^{-14}	0.4582	0.0010	2.70×10^{-6}	0.7702	0.0015	1.31×10^{-15}	0.4507
n_t (mol)	140	47.702	31.285	21.673				46.917	31.508	22.030
β		0.4739	0.3108	0.2153	0.4843	0.3780	0.1377	0.4670	0.3136	0.2193

the water-rich phase "aqueous" and the hydrocarbon-rich phase "organic". Both Stateva and Wakeham (1997), and Castier et al. (1989) use chemical equilibrium constants from different sources. Results, especially compositions, are closer to those reported by Castier et al. (1989) for the 2-phase as well as the 3-phase mixture.

3.7. Convergence and speed

Convergence rate was examined for the initialization procedure as well as the main algorithm. In Figures 7a, 7b and 7c, convergence at the pseudo-reactive azeotrope of MTBE synthesis is tested. Initializing the calculations

follows a quadratic convergence rate (minimization of Q function, Eq. 31). The single-phase reaction requires a small number of iterations. Stability identifies that a second phase will decrease the Gibbs energy and the 2-phase system requires almost three times as many iterations as the single-phase. A more complete description of the convergence in this system is given by the inner loop iterations for each outer loop non-ideality update. The closer to the solution we are, the fewer Newton iterations are required for the inner loop convergence. For cyclohexane synthesis in Figure 7d, fewer components result in a smaller number of iterations. Convergence for the system with the largest number of components and phases, methanol synthesis, is presented in Figure 7e. In contrast to the previous systems, the number of total iterations decreases with the number of phases present in the system. Methanol single-phase synthesis required the maximum number of iterations for all the systems in this work. In general, the iteration number is sensible, especially when it concerns a linearly convergent procedure. It has to be noted that none of the calculations failed to find the equilibrium compositions. As a result, the algorithm is robust, even for computationally demanding VLE or VLLE of non-ideal systems.

The total CPU time required to determine the equilibrium of the systems for selected conditions is reported in Table 8. This time corresponds to the complete procedure including initialization, solving CPE and stability analysis (called after every time a phase set converges). It must be stressed that the time spent to determine the solution is implementation and thermodynamic model dependent for a specific system. For instance, more complex EoS are expected to result in slower calculations compared with a cubic EoS, as PR or SRK. The fastest calculations are for ideal systems, where the outer loop (non-ideality update) is not needed.

For the chemical and phase equilibrium calculation algorithms in the literature, their computational efficiencies are often reported in terms of CPU times and/or iteration numbers. However, it is not always straightforward to compare various algorithms based on these performance indices, because they can be influenced by many factors: The CPU times depend on the hardware, the

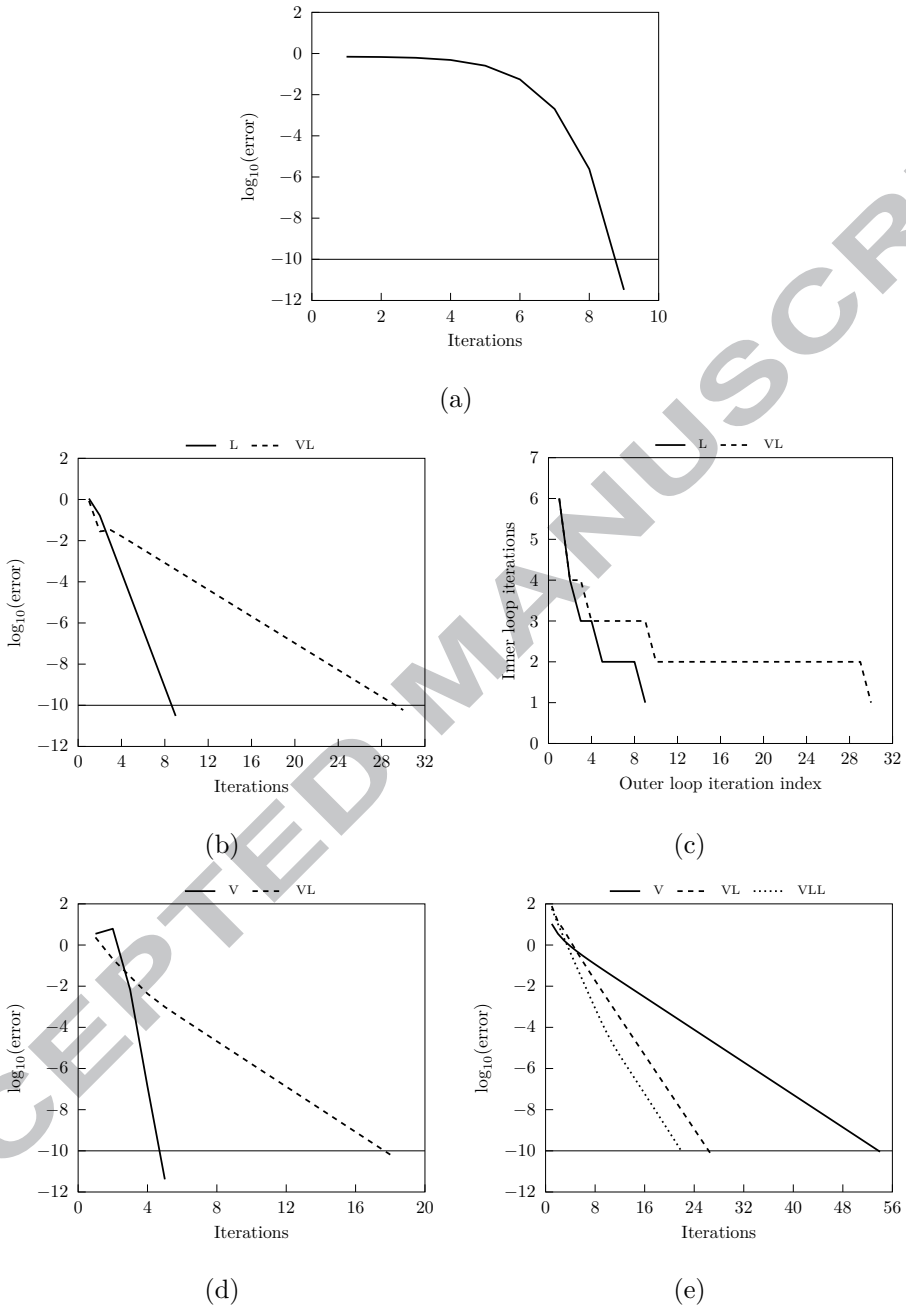


Figure 7: Convergence behavior of MTBE synthesis at 320.92 K and 1 atm (isobutene/methanol 1:1.1) for Q function minimization (a) overall CPE (b), and inner loop (Newton) iterations per outer loop non-ideality updates (c), cyclohexane synthesis at 500 K and 30 atm (d), and 3-phase methanol synthesis at 473.15 K and 101.3 bar (e).

Table 8: CPU time for determining the equilibrium solution of the systems examined (Intel® Core™ i7-5500U CPU@ 2.40 GHz).

System	T (K)	p	$\mathbf{n}_F$ (mol)	CPU time (ms)	Notes
Formaldehyde/water	310	1 atm	$[1\ 1\ 0\ 0]^{\mathrm{T}}$	1.28	Ideal V & L
Xylene separation	350	0.05 atm	$[1\ 1\ 0\ 0\ 0\ 1]^{\mathrm{T}}$	1.31	Ideal V & L
MTBE synthesis	320.92	1 atm	$[1\ 1.1\ 0\ 0]^{\mathrm{T}}$	1.87	Ideal V, Wilson for L
Acetic acid/ethanol esterification	355	1 atm	$[1\ 1\ 0\ 0]^{\mathrm{T}}$	1.72	Ideal V, UNIQUAC for L
Cyclohexane synthesis	500	30 atm	$[1\ 3.05\ 0]^{\mathrm{T}}$	1.48	PR
Methanol synthesis	473.15	101.3 bar	$[15\ 8\ 74\ 30\ 3\ 0\ 10]^{\mathrm{T}}$	3.08	SRK

computer language used, and the compiler; the iteration numbers depend on the initial estimates and the tolerances for the convergence criteria. Furthermore, the cost for single iteration can be very different for different algorithms. Nevertheless, we provide below a comparison of CPU times or iteration numbers with some reported values in the literature. The readers should consider the differences in the factors that may influence the CPU times or iteration numbers in the following comparison:

- MTBE synthesis (Castier et al., 1989)

  The authors use a method consisting of initialization steps with direct substitution accelerated by the General Dominant Eigenvalue Method (GDEM) (Crowe and Nishio, 1975) and Murray's minimization for final convergence. They suggested 5 direct substitution iterations followed by 1 GDEM step for the single-phase chemical equilibrium, 2 GDEM steps for two-phase systems and 3 GDEM steps for three-phase systems (unless certain criteria are met to enter Murray's minimization). The Murray steps are used only for the final convergence, thus are very efficient.

  Their calculations for this system are at different conditions from this work: temperatures corresponding to the two-phase region at 5.07 bar with 1-butene as inert, instead of n-butane. They reported 2 Murray iterations for the single-phase convergence and 1 Murray iteration for the two-phase system. No further information was given for the initialization iterations. Our calculations required 9 outer loop iterations (with a total of 25 Newton

iterations) to converge the liquid phase and 30 outer loop iterations (with a total of 73 Newton iterations) to converge the vapor-liquid system. The authors can reach quadratic convergence rates, and therefore their method is expected to be faster than the algorithm presented here.

- Cyclohexane synthesis (Burgos-Solórzano et al., 2004)

  The authors use a validation tool, a deterministic mathematical method that guarantees finding the global minimum of the Gibbs energy. They reported 120 ms required for the validation tool calculations [Sun Blade 1000 Model 1600 (600 MHz) workstation], whereas we spent 1.5 ms for the complete calculations (initialization, convergence of single phase, stability analysis, convergence of two-phase system and final stability analysis).

- Acetic acid/ethanol esterification (Xiao et al., 1989; Castier et al., 1989)

  Xiao et al. (1989) compared two stoichiometric methods, the S-C and the KZ algorithm. The S-C algorithm is the classical stoichiometric approach using nested loops. Its inner loop solves the phase equilibrium problem (flash) using a successive substitution approach based on the Rachford-Rice equation, while its outer loop updates the extents of reaction. The KZ algorithm, proposed as an improvement of the S-C algorithm, switches the outer and inner loops in the S-C algorithm. They reported 10 outer loop iterations (with a total of 42 Newton iterations) for the S-C algorithm and 9 outer loop iterations (with a total of 23 Newton iterations) for the KZ algorithm. In our work, after 8 Newton iterations of the initialization procedure, the solution obtained coincides with the single vapor phase solution and the main solver was not needed. For the VLE of this reaction system we needed 44 outer loop iterations (with a total of 106 Newton iterations). In Xiao et al. (1989), the initial assumption is a two-phase system. Since all the three algorithms (S-C, KZ and ours) are supposed to show an overall linear convergence, their iteration numbers should in principle be comparable. We note that in Xiao et al. (1989) a very loose tolerance is used for the convergence, $\sum_{i=1}^{N_C}(k_i^{\text{new}}/k_i - 1)^2 < 10^{-6}$, where

$k_i = y_i/x_i$. In our solution, a much tighter convergence criterion is used (Eq. 39).

Castier et al. (1989) used a slightly higher temperature than the one presented in this work: 358.15 K. The ideal gas assumption for the vapor phase resulted in a single vapor phase at equilibrium that required 3 Murray iterations. On the other hand, using an EoS that accounts for the acid dimerization in the vapor phase, convergence required 3 Murray iterations for the initially assumed single vapor phase and 2 Murray iterations for the final vapor-liquid system.

- Methanol synthesis (Castier et al., 1989)

  For the three-phase synthesis, all phase sets are initialized in Castier et al. (1989): L, VL and VLL required 5 iterations with 1 GDEM step, 10 iterations with 2 GDEM steps, and 12 iterations with 2 GDEM steps respectively (the third GDEM step was not needed for the three-phase convergence). The Murray iterations to converge L, VL and VLL systems were 3, 4 and 1 respectively. We needed 10 Newton iterations for the initialization of the single-phase system, and after stability introduced additional phases, we did not initialize again. For our CPE calculations, we needed 54 outer loop iterations (with a total of 149 Newton iterations) for V, 27 outer loop iterations (with a total of 78 Newton iterations) for VL and 22 outer loop iterations (with a total of 60 Newton iterations) for VLL. In our algorithm, no acceleration was implemented.

3.8. Alternative treatment

We have minimized Q function (Eq. 31) for a single ideal phase to initialize $\boldsymbol{\lambda}$ for the nested-loop calculations, by keeping the phase amount at a fixed value. Alternatively, this minimization could be attempted considering a set of non-ideal phases ($N_P > 1$), where the fugacity/activity coefficients are assumed composition independent. Every time a new phase is introduced, fugacity/activity coefficients are calculated for the current composition estimate

and kept constant during the minimization. Because $\nabla^2 Q$ is still positive definite, finding the unique minimizer is a safe procedure that requires a finite number of iterations.

To reduce the number of iterations, an accelerated successive substitution method could be utilized. The General Dominant Eigenvalue Method (GDEM) (Crowe and Nishio, 1975) is a possible candidate. Although acceleration is needed to enhance the efficiency of calculations, the material balance is one of the working equations, meaning that the independent variables do not obey it at every iteration. As a result, the values of $G = f(\boldsymbol{\lambda}, \mathbf{n}_t)$ cannot be used to validate, if the acceleration actually leads to a decrease in the Gibbs energy.

The RAND approach (White et al., 1958; Greiner, 1991; Michelsen and Mollerup, 2007) can also be used to increase the convergence rate. The method of Lagrange multipliers discussed in this work can be employed as initial converging steps, before switching to the quadratically convergent RAND algorithm. We will discuss how to apply the RAND approach to non-ideal multiphase and multiple reaction systems in a separate paper.

In a completely different formulation of the problem, the Gibbs energy is minimized with respect to extents of reactions ξ_r under the non-negativity constraint:

$$\begin{aligned} &\min_{\boldsymbol{\xi}} G(T, p, \boldsymbol{\xi}) \\ \text{s.t.} \quad & n_{ik} \geq 0, \quad i = 1, ..., N_C \qquad k = 1, ..., N_P \end{aligned} \tag{57}$$

where

$$\sum_{k=1}^{N_P} n_{ik} = n_{F,i} + \sum_{r=1}^{N_R} \nu_{ir} \xi_r \tag{58}$$

If we do not account directly for the non-negativity constraints, this formulation is essentially an unconstrained minimization problem and can be advantageous for a small number of reactions. However, there are initialization problems and the method is prone to round-off errors. To overcome this obstacle, we can select N_E components as the "optimum" basis, the primary components, which are

the most abundant in the system (Michelsen and Mollerup, 2007). The rest of the components are called secondary and their mole numbers can be found from those of the primary components. A number of publications has addressed the issue of selecting the proper basis (Brinkley, 1946, 1947; Prigogine and Defay, 1947; Schott, 1964). The conventional treatment involves the solution of a PT-flash in a nested loop and the update of the extents of the reactions in the outer loop. Two different stoichiometric algorithms are given in Castier et al. (1989), and Phoenix and Heidemann (1998).

4. Conclusions

An extended algorithm for simultaneous chemical and phase equilibrium calculations based on Michelsen (1989) and Michelsen and Mollerup (2007) was presented. The procedure involves a nested-loop scheme and calculations begin by assuming a single-phase reaction system. The initialization method allows for better quality initial estimates, while stability analysis guarantees finding the Gibbs energy global minimum, by sequentially introducing new phases that can lower the system Gibbs energy. CPE was successfully calculated for a number of systems described by different thermodynamic models. The convergence rate is linear, due to the successive substitution in the outer loop. Nevertheless, the method appears to be robust, without failing solving CPE for all the systems examined.

Acknowledgments

We would like to acknowledge the help of Prof. Michael L. Michelsen for his insightful comments and suggestions.

References

Abrams, D.S., Prausnitz, J.M., 1975. Statistical thermodynamics of liquid mixtures: A new expression for the excess gibbs energy of partly or completely miscible systems. AIChE Journal 21, 116–128.

Barbosa, D., Doherty, M.F., 1988. The influence of equilibrium chemical reactions on vapor-liquid phase diagrams. Chemical Engineering Science 43, 529–540.

Bonilla-Petriciolet, A., Rangaiah, G.P., Segovia-Hernández, J.G., 2011. Constrained and unconstrained Gibbs free energy minimization in reactive systems using genetic algorithm and differential evolution with tabu list. Fluid Phase Equilibria 300, 120–134.

Bonilla-Petriciolet, A., Segovia-Hernández, J.G., 2010. A comparative study of particle swarm optimization and its variants for phase stability and equilibrium calculations in multicomponent reactive and non-reactive systems. Fluid Phase Equilibria 289, 110–121.

Bonilla-Petriciolet, A., Vázquez-Román, R., Iglesias-Silva, G.A., Hall, K.R., 2006. Performance of stochastic global optimization methods in the calculation of phase stability analyses for nonreactive and reactive mixtures. Industrial & Egineering Chemistry Research 45, 4764–4772.

Brinkley, Jr, S.R., 1946. Note on the conditions of equilibrium for systems of many constituents. The Journal of Chemical Physics 14, 563–564.

Brinkley, Jr, S.R., 1947. Calculation of the equilibrium composition of systems of many constituents. The Journal of Chemical Physics 15, 107–110.

Burgos-Solórzano, G.I., Brennecke, J.F., Stadtherr, M.A., 2004. Validated computing approach for high-pressure chemical and multiphase equilibrium. Fluid Phase Equilibria 219, 245–255.

Castier, M., Rasmussen, P., Fredenslund, A., 1989. Calculation of simultaneous chemical and phase equilibria in nonideal systems. Chemical Engineering Science 44, 237–248.

Crowe, C.M., Nishio, M., 1975. Convergence promotion in the simulation of chemical processes - the general dominant eigenvalue method. AIChE Journal 21, 528–533.

Floudas, C.A., Visweswaran, V., 1990. A global optimization algorithm (GOP) for certain classes of nonconvex NLPs–I. Theory. Computers & Chemical Engineering 14, 1397–1417.

Fredenslund, A., Jones, R.L., Prausnitz, J.M., 1975. Group-contribution estimation of activity coefficients in nonideal liquid mixtures. AIChE Journal 21, 1086–1099.

Gautam, R., Seider, W.D., 1979a. Computation of phase and chemical equilibrium: Part I. Local and constrained minima in Gibbs free energy. AIChE Journal 25, 991–999.

Gautam, R., Seider, W.D., 1979b. Computation of phase and chemical equilibrium: Part II. Phase-splitting. AIChE Journal 25, 999–1006.

Gautam, R., Seider, W.D., 1979c. Computation of phase and chemical equilibrium: Part III. Electrolytic solutions. AIChE Journal 25, 1006–1015.

Gautam, R., Wareck, J.S., 1986. Computation of physical and chemical equilibria–alternate specifications. Computers & Chemical Engineering 10, 143–151.

George, B., Brown, L.P., Farmer, C.H., Buthod, P., Manning, F.S., 1976. Computation of multicomponent, multiphase equilibrium. Industrial & Engineering Chemistry Process Design and Development 15, 372–377.

Greiner, H., 1991. An efficient implementation of Newton's method for complex nonideal chemical equilibria. Computers & Chemical Engineering 15, 115–123.

Jalali, F., Seader, J.D., Khaleghi, S., 2008. Global solution approaches in equilibrium and stability analysis using homotopy continuation in the complex domain. Computers & Chemical Engineering 32, 2333–2345.

Jalali-Farahani, F., Seader, J.D., 2000. Use of homotopy-continuation method in stability analysis of multiphase, reacting systems. Computers & Chemical Engineering 24, 1997–2008.

Maurer, G., 1986. Vapor-liquid equilibrium of formaldehyde-and water-containing multicomponent mixtures. AIChE Journal 32, 932–948.

McDonald, C.M., Floudas, C.A., 1995. Global optimization for the phase and chemical equilibrium problem: Application to the NRTL equation. Computers & Chemical Engineering 19, 1111–1139.

McDonald, C.M., Floudas, C.A., 1997. GLOPEQ: A new computational tool for the phase and chemical equilibrium problem. Computers & Chemical Engineering 121, 1–23.

Michelsen, M.L., 1982. The isothermal flash problem. Part I. Stability. Fluid Phase Equilibria 9, 1–19.

Michelsen, M.L., 1989. Calculation of multiphase ideal solution chemical equilibrium. Fluid Phase Equilibria 53, 73–80.

Michelsen, M.L., Mollerup, J.M., 2007. Thermodynamic Models: Fundamentals & Computational Aspects. Second ed., Tie-Line Publications, Holte, Denmark.

Moodley, K., Rarey, J., Ramjugernath, D., 2015. Application of the bio-inspired Krill Herd optimization technique to phase equilibrium calculations. Computers & Chemical Engineering 74, 75–88.

NIST Chemistry WebBook, Accessed: 19.02.2016. NIST Standard Reference Database Number 69. http://webbook.nist.gov/cgi/cbook.cgi?ID=C106978&Mask=4.

Peng, D.Y., Robinson, D.B., 1976. A new two-constant equation of state. Industrial & Engineering Chemistry Fundamentals 15, 59–64.

Pérez Cisneros, E.S., Gani, R., Michelsen, M.L., 1997. Reactive separation systems–I. Computation of physical and chemical equilibrium. Chemical Engineering Science 52, 527–543.

Phoenix, A.V., Heidemann, R.A., 1998. A non-ideal multiphase chemical equilibrium algorithm. Fluid Phase Equilibria 150–151, 255–265.

Prigogine, I., Defay, R., 1947. On the number of independent constituents and the phase rule. The Journal of Chemical Physics 15, 614–615.

Rao, Y.K., 1985. Extended form of the Gibbs phase rule. Chemical Engineering Education 19, 46–49.

Saito, S., Michishita, T., Maeda, S., 1971. Separation of meta- and para-xylene mixture by distillation accompanied by chemical reactions. Journal of Chemical Engineering of Japan 4, 37–43.

Schott, G.L., 1964. Computation of restricted equilibria by general methods. The Journal of Chemical Physics 40, 2065–2066.

Smith, W.R., Missen, R.W., 1982. Chemical Reaction Equilibrium Analysis: Theory and Algorithms. Wiley, New York, United States of America.

Soave, G., 1972. Equilibrium constants from a modified Redlich-Kwong equation of state. Chemical Engineering Science 27, 1197–1203.

Stateva, R.P., Wakeham, W.A., 1997. Phase equilibrium calculations for chemically reacting systems. Industrial & Engineering Chemistry Research 36, 5474–5482.

Ung, S., Doherty, M.F., 1995a. Calculation of residue curve maps for mixtures with multiple equilibrium chemical reactions. Industrial & Engineering Chemistry Research 34, 3195–3202.

Ung, S., Doherty, M.F., 1995b. Necessary and sufficient conditions for reactive azeotropes in multireaction mixtures. AIChE Journal 41, 2383–2392.

Ung, S., Doherty, M.F., 1995c. Synthesis of reactive distillation systems with multiple equilibrium chemical reactions. Industrial & Engineering Chemistry Research 34, 2555–2565.

Ung, S., Doherty, M.F., 1995d. Theory of phase equilibria in multireaction systems. Chemical Engineering Science 50, 3201–3216.

Ung, S., Doherty, M.F., 1995e. Vapor-liquid phase equilibrium in systems with multiple chemical reactions. Chemical Engineering Science 50, 23–48.

Wasylkiewicz, S.K., Ung, S., 2000. Global phase stability analysis for heterogeneous reactive mixtures and calculation of reactive liquid-liquid and vapor-liquid-liquid equilibria. Fluid Phase Equilibria 175, 253–272.

White, III, C.W., Seider, W.D., 1981. Computation of phase and chemical equilibrium: Part IV. Approach to chemical equilibrium. AIChE Journal 27, 466–471.

White, W.B., Johnson, S.M., Dantzig, G.B., 1958. Chemical equilibrium in complex mixtures. The Journal of Chemical Physics 28, 751–755.

Wilson, G.M., 1964. Vapor-liquid equilibrium. xi. a new expression for the excess free energy of mixing. Journal of the American Chemical Society 86, 127–130.

Xiao, W.d., Zhu, K.h., Yuan, W.k., Chien, H.H.y., 1989. An algorithm for simultaneous chemical and phase equilibrium calculation. AIChE Journal 35, 1813–1820.

Zeleznik, F.J., Gordon, S., 1968. Calculation of complex chemical equilibria. Industrial & Engineering Chemistry 60, 27–57.

Highlights

- Equilibrium calculation of multiphase systems in presence of chemical reactions
- Robust variable initialization and stability analysis for equilibrium verification
- Successful calculations of two- and three-phase reaction systems
- Coupling with a second-order method can improve computation efficiency